A new high-resolution X-ray spectrometer for studying electronic dynamics

Non-resonant inelastic X-ray scattering (NRIXS) is an interesting tool for spectroscopic investigations, with access to large momentum transfers allowing investigation beyond the dipole limit, and over atomic scale correlation lengths. NRIXS with ~eV resolution has been used to investigate valence structure, particle-hole excitations and plasmons. However, the method has significant practical constraints and it is only relatively recently that experimental work has begun to focus on narrower electronic (non-phonon) spectral features at ~eV energy transfers [1]. This, in large part, is due to instrumental limitations, as one needs both high resolution and high spectral intensity. However, given the possibility to directly investigate transitions of d electrons and the dispersion of such excitations (e.g., orbitons) there is significant interest.

Non-resonant scattering offers some advantages relative to resonant inelastic X-ray scattering (RIXS). NRIXS is *relatively* simple to interpret and calculate as the NRIXS cross section responds directly to the electronic charge density of the initial and final states via the non-resonant $\boldsymbol{A}^2$ term of the interaction Hamiltonian: avoiding the intermediate states from the resonant interaction, the $\boldsymbol{A}\cdot\boldsymbol{p}$ term, reduces count-rates but simplifies interpretation. The choice of X-ray energy in a non-resonant experiment is flexible, so it can be chosen to optimize optical performance to facilitate improved resolution. The energy can also be chosen to be relatively high to improve transmission into and out-of sample environments, and to increase the illuminated volume of a sample.

Here we used analyzers with a controlled temperature gradient (TG) [2] to allow good, 25 meV, resolution with a single element detector with a large space near the sample. The main elements of the spectrometer are shown in Fig. 1(a), and include the medium resolution monochromator, a bent cylindrical focusing mirror, stages and environment for the sample, and the analyzer system on the two-theta arm (Fig. 1(b)). This is installed at SPring-8 **BL43LXU** [3]. The operating energy of the spectrometer is 15816 eV, corresponding to the energy of the Si (888) back-reflection analyzer crystals. A TG of ΔT_g = 1.32 K/80 mm was applied over the analyzer with improvement as seen in the inset in Fig. 2(a), even using a single element detector placed 20 cm from the sample.

We use the new spectrometer to investigate a band of *d-d* excitations in NiO as we increase the temperature from 20 to 800 K, through the Neel point at T_N = 523 K [2]. The NiO crystal was placed inside of a closed-cycle cryofurnace. Measurements were done at **Q** = (2.5 2.5 2.5) reciprocal lattice units (rlu), $|\mathbf{Q}|$ = 6.52 Å^{-1}, with the acceptance of the analyzer being $\Delta\mathbf{Q}$ = (0.05 0.22 0.22) rlu. This **Q** is near the maximum intensity for this band of excitations.

The measured spectra are shown in Figs. 2(b) and 3(a), after background subtraction. At low temperatures, some structure is evident, and the

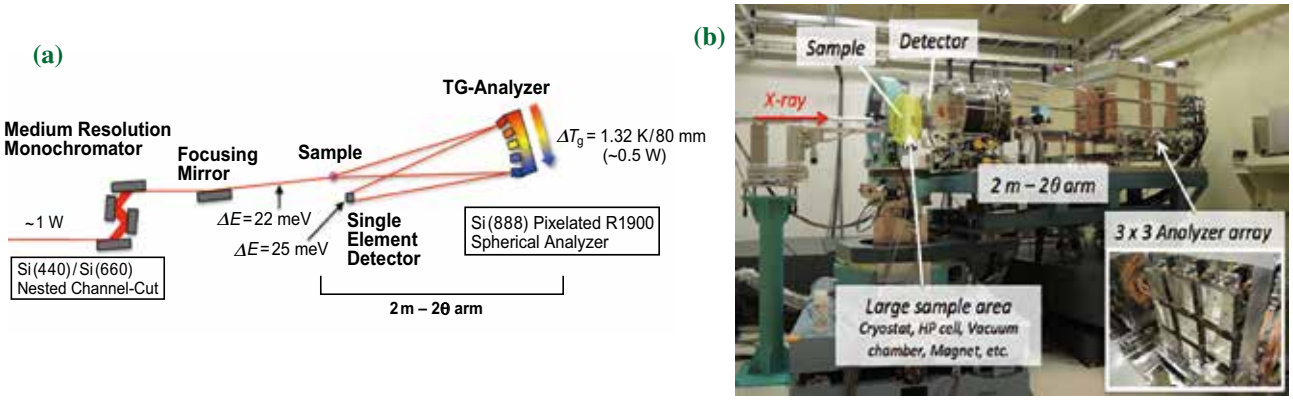

Fig. 1. 25 meV resolution Non-resonant IXS spectrometer with temperature-gradient (TG) analyzer. **(a)** Schematic showing the main components. **(b)** Photo of the spectrometer.

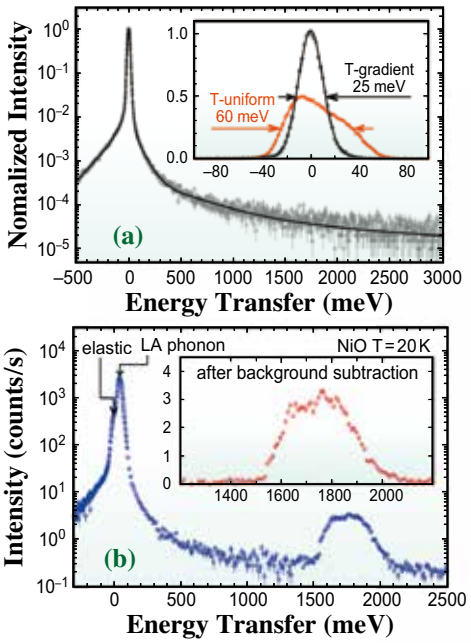

Fig. 2. Spectrometer response. **(a)** Measured scattering, with the TG, from plexiglass at its structure factor maximum where its response is predominantly elastic. The inset shows the resolution with and without TG. **(b)** The *d-d* excitation in NiO appears clearly above background.

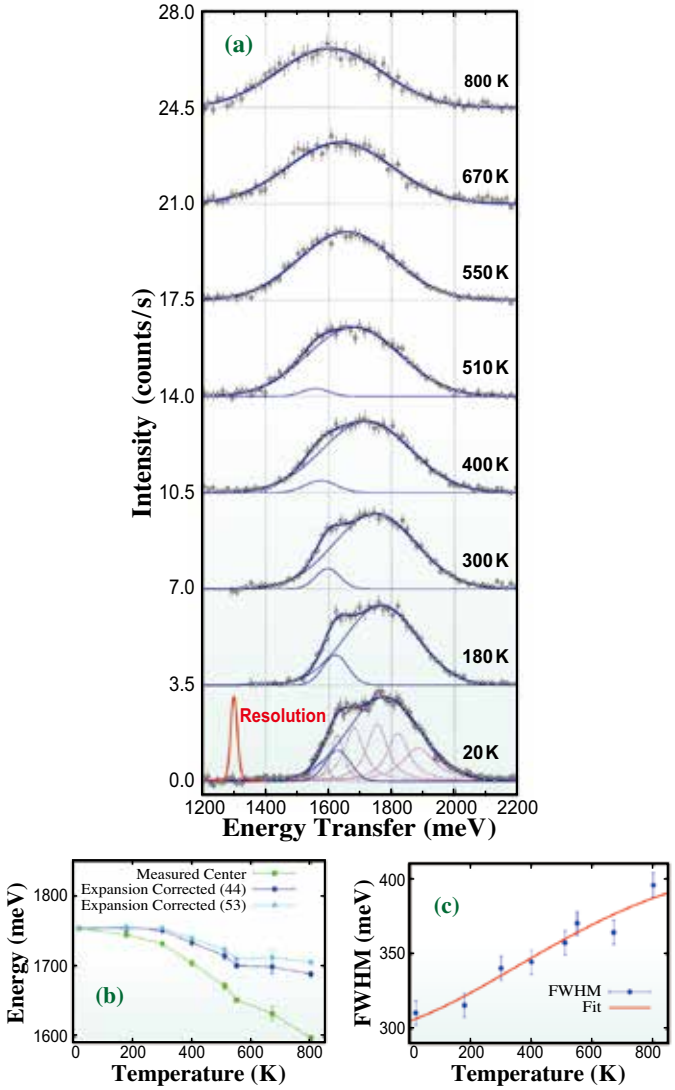

Fig. 3. **(a)** Temperature dependence of the *d-d* spectra of NiO measured at Q = (2.5 2.5 2.5) rlu. One TG analyzer (0.0024 sr) and single element detector 2×2 mm^2 were used. **(b,c)** Temperature dependence of the *d-d* excitation parameters. (b) Line position before and after correction for thermal expansion, using either the calculated value for the energy change (44 meV/pm) or the experimental value (53 meV/pm, see Ref. 2). Solid lines are guides for the eye. (c) Width of the excitation compared to the model in Ref. 2.

spectra can be fit using two Gaussian lines, or a more complex multiplet to reproduce all of the fine structure. At higher temperatures the response broadens, shifts to lower energies, and becomes increasingly Gaussian. The temperature dependence of the center and width of the response are shown in Figs. 3(b) and 3(c). The energy decreases steeply in the neighborhood of the Neel point, and then continues to drop (Fig. 3(b)). The width increases approximately linearly with temperature (Fig. 3(c)).

This data is the first to show the impact of phonons on electronic excitations: the linewidth increase is well fit using a simple model of thermally induced fluctuations with a scale factor of 53(3) meV energy shift per pm of Ni-O lattice constant expansion (solid line in Fig. 3(c)). Applying the same value for the thermal expansion then allows the Neel point to be more clearly observed in the temperature-induced shift of the center of the response (Fig. 3(b)). The experimental value of 53(3) meV is in reasonable agreement with the 44.5 meV/pm estimated from *ab initio* ligand field theory [4].

This work demonstrates the potential of a new high-resolution spectrometer now coming on line at the RIKEN SPring-8 Center.

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